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What Determines the Martensitic Transition Temperature in Alloys?

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The intriguing puzzle is addressed concerning the dramatic dependence generally observed of the Martensitic transition temperature on the composition of alloys. Based on one of the simplest possible systems, the Ti$_x$Zr$_{1-x}$ alloy system, a theory is developed including the effect of a disorder scattering of the phonons due to a mass difference between the elements. The depression of the Martensitic transition temperature, $\Delta M_s$, is shown to depend parabolically on concentration $c$, as $c(1-c)$, for small depressions. For larger $\Delta M_s$ an enhancement at intermediate $c$ is predicted. This gives rise to a more triangular dependence as a function of $c$. The theory contains only one phenomenological parameter. Comments are given relevant for other more complicated alloy systems.

1. INTRODUCTION

In practically interesting Martensitic materials the transition temperature is often close to room temperature. It is surprisingly easy to obtain a large range of transition temperatures, $M_s$ in the complicated alloys of three or more components. The question is why the transition temperature is so dramatically dependent on the alloy composition? The effect is much larger than conceivable from estimated consequences of changes in the electronic effects, in the inter atomic forces, in atomic radii or as a result of atomic ordering. In the complicated alloys, as for example Ni$_x$Ti$_{1-x}$ [1] and Cu$_3$AlBe$_4$ [2] a dramatic change in $M_s$ is observed for $x \approx 0.5$ and $\epsilon \approx 0$. In these interesting systems probably all the mentioned effects play a role, but still it is hard to understand the strong influence on $M_s$. A model including electronic effects was proposed [3] for the ternary NiTi-based alloys providing an interpolation formula between two elements of the type NiTi and $M_x$Ti, where $M_x$ is an element which forms the B2 structure with Ti. Is was possible to account for a small downward deviation from a linear interpolation of $M_s$ between the two pure systems, using two essentially free parameters (and including temperature influence on the electrons). However, in that model one totally neglects the thermal nature of the Martensitic transformation; and in most cases it is a high temperature transformation compared to the natural energy scale, the Debye temperature.

In order to get a deeper understanding let us turn to the simplest possible model systems, the pure group-IV elements, which have been intensively studied both experimentally and theoretically. For Zr it was demonstrated that an accurate first principles band structure calculation [4] gives the hcp structure as the stable structure at $T = 0$, i.e. from purely electronic considerations. It was
also demonstrated that the inclusion of anharmonic effects was necessary, and sufficient to stabilize the bcc structure at high temperatures. No similar calculations have been made for pure Ti, but detailed neutron scattering measurements have been made for both Ti [5] and Zr [6]. The phonon spectra for the bcc phase at the same temperature are identical apart from a scale factor which is square root of the ratio of the masses $(m_{Zr}/m_{Ti})^{1/2}$. Since the phonon frequency is proportional to $(f_i/m)^{1/2}$ it shows that the force constants, $f_i$, i.e. the interatomic forces for the two metals are identical. However, the masses are different by a factor of $\approx 2$, since $m_{Ti} = 47.90$ and $m_{Zr} = 91.22$. The metals are very close in chemical respect and consequently they form ideal mixtures for all concentrations and all temperatures. This means that if there is a tendency to form stoichiometric, ordered alloys the ordering energy is small. Thus the ordering temperature is so low that the diffusion kinetics is too slow for ordered structures to form. The alloy system is also well documented [1] and shows that the melting temperatures are almost independent of concentration: $T_{melting}^{Ti} = 1860^\circ C$ and $T_{melting}^{Zr} = 1720^\circ C$, interpolating almost linearly in the alloys with a small depression of only about 100°C, or by only 5%. The Martensitic transition temperatures are also almost identical: $M_a^{Ti} = 882^\circ C$ and $M_a^{Zr} = 865^\circ C$, differing by only 1.5%. One could then, based on the above mentioned electronic effects, expect that $M_s$ in the alloy would follow a linear interpolation and fall within $882 - 865^\circ C$. On the contrary $M_s$ decreases by about a factor of two at the 50-50% concentration to $M_s = 500^\circ C$. The intriguing data for $M_s$ in the Ti - Zr alloy system [1] are shown in Fig.1.

In the next section we will seek an explanation for the paradox of the remarkable dependence of $M_s$ on alloying. The suggested mechanism is most probably also of relevance for the more complicated situations in ternary alloys or binary alloys of very different metals.

![Fig.1. Martensitic transition temperature for the Ti - Zr alloy system [1].](image)

### 2. DISORDER MODEL FOR DEPRESSION OF $M_s$ IN ALLOYS

The Ti – Zr alloy system represents a perfect example of a model of an alloy between two identical elements with the same $M_s^{pure}$, only differing in the atomic masses by a factor of two. Such models have been considered by perturbation theory for small concentrations $c$ [7] to first order in $c$. No rigorous results exist for large $c$, however Ziman [8] rationalizes the physically appealing result, that the phonon damping must be proportional to $c(1 - c)$, which is symmetric in the alloy elements. For both Ti and Zr there is already a considerable anharmonic frequency shift $\Delta\nu$ and damping $\Gamma$ at
We remark that $M_s = 1138^\circ Zr - 1155^\circ Ti K$ is large compared to the Debye temperatures for both the bcc and the hcp phases, which for Ti are $[5] \Theta_{D}^{hcp} = 360 K$ and $\Theta_{D}^{bcc} = 290 K$. Thus in our case we have $M_s^\text{pure} = 3.4 \Theta_D$. The anharmonic scattering of phonons is due to the lattice distortions created by other phonons being present, while a studied phonon is propagating through the lattice. The large wave length phonons tend to see only the average structure and are therefore not much influenced by small scale distortions of the neighbor distances. On the other hand the small wave length (or zone boundary $q$-vector) phonons are strongly effected, since the distortions are on the same length scale. Effectively, the distortions change the inter atomic forces seen by the small wave length phonons. The mass-disorder scattering behaves in a similar way with respect to the wave length. The only essential difference is that the mass-disorder is temperature induced.

We shall now analyze the effect of additional mass-disorder scattering of the phonons. Let us assume it gives rise to an additional shift $\Delta_q \rightarrow \Delta_q + \delta_q$ and damping $\Gamma_q \rightarrow \Gamma_q + \gamma_q [9]$. The imaginary part of the phonon Greens function $[10]$ can then be written, expanding the denominator to first order in $\delta_q$ and $\gamma_q$

$$\text{Im} G_q(\omega) = \frac{2\omega_q(\Gamma_q + \gamma_q)}{\pi(\omega_q^2 - \omega^2)^2 + 4\omega^2(\Gamma_q + \gamma_q)^2 + 4\omega_q(\omega_q^2 - \omega^2)\delta_q + 2\omega_q\Gamma_q\gamma_q} \approx \left(1 - \frac{\gamma_q}{\Gamma_q}\right) \text{Im} G_q(\omega),$$

(1)

where $\omega_q = \omega_q^0 + \Delta_q$ includes the anharmonic shift, and the last expression is obtained by expanding near the resonance $\omega = \omega_q$. The anharmonic damping is of the form $[10]$

$$\Gamma_q = \frac{18\pi}{h^2} \sum_{k,k'} |V_\beta(q,k,k')|^2 \{ (n_k + n_{k'}) \delta(\text{energy}) + (n_k - n_{k'}) \delta(\text{energy}) \},$$

(2)

where $V_\beta$ is the third derivative of the anharmonic potential and $n_q = \left[e^{\beta\omega_q} - 1\right]^{-1}$ is the phonon population factor, $\beta = 1/(k_B T)$; the $\delta$-functions conserve the energy in the scattering processes (for simplicity of notation we set $h = 1$ in the following). For large temperature $T \gg \Theta_D$ the phonon population is large $n_q \gg 1$ and $n_q \approx 1/(\beta\omega_q)$. For Zr the Debye temperature is $\Theta_D^{Zr} = 210 K$ and at $T = M_s$ the population of the highest frequency phonons is $n \approx 5$. The population is even higher, $n \approx 20$, in the low frequency ‘valley’ along the [112] wave vector direction, which always seem to exist in the elastically highly anisotropic Martensitic materials. On the other hand the mass-disorder induced damping is independent of temperature and proportional to $c(1 - c) [8]$ and the mass difference $\Delta m = m^{Zr} - m^{Ti}$ squared. Accordingly, displaying only the most important features

$$\frac{\gamma_q}{\Gamma_q} = \beta c(1 - c) |f_q|^2.$$  

(3)

This correction is largest in the phase where the anharmonic damping is small, i.e. in the hcp phase. We have introduced a $q$-dependent ratio $|f_q|^2$ of the mass-disorder and the anharmonic scattering, which is difficult to calculate. Since the scattering mechanisms treat the long and short wave length phonons similarly, we expect that $|f_q|^2$ is not very strongly $q$-dependent and is proportional to $\Delta m^2$.

The free energy $F$ can be calculated from the internal energy $\langle \mathcal{H} \rangle$ by integrating the exact relation

$$\frac{d}{d\beta} (\beta F) = \langle \mathcal{H} \rangle_\beta.$$  

(4)

The average of the Hamiltonian $\langle \mathcal{H} \rangle = \sum_q \omega_q (n_q + \frac{1}{2})$ is related to $\text{Im} G_q(\omega)$ $[11]$. The mass-disorder correction to the internal energy is from eq.(1) and eq.(3) then found to be of the form

$$\Delta \langle \mathcal{H} \rangle = -c(1 - c) \sum_q |f_q|^2 \int_{-\infty}^{\infty} \frac{1}{e^{\beta\omega} - 1} \beta \omega^2 \text{Im} G_q(\omega)/\omega \, d\omega \approx c(1 - c) \frac{1}{2} \beta \sum_q |f_q|^2 \langle \omega_q^2 \rangle,$$  

(5)

where we have made a high temperature expansion and introduced the second moment of the phonon spectrum $\langle \omega_q^2 \rangle$ (assuming that odd moments are zero, no other terms exist). In the presence of anharmonicity $\langle \omega_q^2 \rangle$ might be significantly larger than $(k_B \Theta_D)^2$. The coefficient to $c(1 - c)$ in eq.(5) is
therefore quite large at $T = M''$, corresponding to a few OD. We can now from eq.(4) calculate the free energy difference between the hcp and the bcc phases in the presence of the mass-disorder scattering. It has the following simple form, reflecting the ratio between the disorder and the anharmonic scattering power

$$F_{\text{hcp}} - F_{\text{bcc}} = c(1-c)\frac{a}{T} \Delta S_{\text{disorder}} = (M_{s}^{\text{pure}} - T)\Delta S_{\text{pure}}.$$ (6)

In the last equation we have equated the disorder induced free energy difference to the temperature dependent free energy difference between the pure phases. This temperature dependence is assumed to be given by the entropy term $T\Delta S_{\text{pure}} = T(S_{\text{bcc}} - S_{\text{hcp}})$. The Martensitic temperature for the alloy $M_{\text{alloy}}^{\text{pure}}$ is obtained as the solution for $T$ to eq.(6). In the case of a small depression we can insert $T = M_{s}^{\text{pure}}$ on the left hand side and we simply find

$$\Delta M_{s} = M_{s}^{\text{pure}} - M_{\text{alloy}} \propto c(1-c)M_{s}^{\text{pure}}.$$ (7)

This gives a parabolic depression, as may be expected intuitively. However, when the depression is large, i.e. $T$ gets smaller, there is an enhancement effect of the left hand side, as is clear from eq.(6). This enhances the large depression regions even further. Thus one gets a more 'triangular' dependence on the concentration. This is in fact observed as seen in Fig.1. This remarkable behavior is here explained by eq.(6) in terms of just one phenomenological parameter $p = a/\Delta S_{\text{pure}}$.

3. DISCUSSION

The characteristic features of the behavior of $M_{s}$, Fig.1., can thus be understood as a mass-disorder effect. However, we can go a step further and understand that asymmetries will arise in the concentration dependence if the anharmonic damping is different in the two pure materials [9]. The depression is smallest when there is already a large anharmonic scattering. According to Petry et al [5, 6] the damping is larger in $Ti$ than in $Zr$ at $T = M_{s}$, $M_{s}^{\text{pure}}$. We therefore expect a slight enhancement of the depression for the $Zr$ rich alloys. Fig.1. shows the expected shift of the minimum toward $Zr$.

In the above arguments we have assumed the same $M_{s}^{\text{pure}}$ for both elements $A,B$. The result can easily be generalized to the case of different $M_{s}$ values. This is for example the case in systems like the NiTi and $MxTi$ ternary alloys, mentioned in the introduction. Clearly electronic effects, giving rise to different atomic force constants, must now be included. In the simplest approximation, for iso-structural alloys, it would just give rise to a linear interpolation between the different pure temperatures $M_{s}^{A}$ and $M_{s}^{B}$. The disorder scattering effect (in which we can now include both mass-disorder and force-constant-disorder) will generally produce a parabolic-like depression, which may be asymmetric in the concentrations. This is in fact the general feature observed in the mentioned alloys. The present theory is able to qualitatively account for all the observations with $Mx$=$Pd,Pt,Au$, giving a large depression, probably mainly due to the large mass difference $\Delta m = m^{M_{x}} - m^{Ti}$. Also the observed asymmetry is as predicted, since presumably the anharmonicity is larger for the high $M_{s}$ compounds, thus shifting the maximum of the depression toward the low $M_{s}$ compound. The electronic model [3] is able only to account satisfactorily for the NiTi - $PdTi$ ternary alloy system. It is clear that both the disorder and the electronic effects may have to be taken into account.

For alloys of chemically very different elements, which form different stoichiometric, ordered structures, for example Ni$_{x}$Ti$_{1-x}$ and Cu$_{3}$AlBe$_{x}$, the situation is much more complicated. Here, the electronic properties, in particular the electronic densities of states, change rapidly for different ordered phases. However, in addition, the above discussed disorder effect, which is even enhanced due to atomic disorder relative to the preferred order, must be taken into account. In Cu$_{3}$AlBe$_{x}$ the disorder element Be has a very small mass compared to the other elements: $m^{Be} = 9$, $m^{Al} = 27$ and $m^{Cu} = 63.5$. Therefore $\Delta m$ is large and already the mass-disorder effect is large, in addition
Be is chemically very different (divalent) from Al and Cu. Consequently, our theory may contribute substantially to the explanation for Be being such an effective agent with which to depress $M_s$ in Cu_3Al [9].

In this paper we have demonstrated that the disorder scattering of phonons play a large role for determining the Martensitic transition temperature $M_s$, resulting in a general depression of $M_s$ for intermediate concentrations. The disorder essentially weakens the potentially stable hcp phase, whereas it probably stiffens the bcc lattice since $\Delta_q + \delta_q$ increases. Notice the shift $\delta_q$ does not enter into our argument. Experimental measurements of a TiZr alloy would be quite interesting. In fact there exists an early neutron scattering measurement [12] of Ti_{67}Zr_{33} which seem to indicate that the energy $\omega_N \approx 7.8$meV of the potentially soft $N$-point $T_1$ phonon [4, 5] (or soft 'valley') is not softer in the alloy with $M_s^{\text{alloy}} \sim 773K$ than that in the pure systems, $\omega_T = 8.5$meV and $\omega_N = 5$meV at $T = M_s = 1155K$. In particular it would be interesting to observe damping effects and quasi-elastic scattering in the hcp and the bcc phases. Physically we expect that in the depressed regions, for temperatures below $M_s^{\text{pure}}$ the hcp structure will be replaced by short range order of hcp phase, located around concentration fluctuations toward a concentration favoring the hcp phase. In a scattering experiment it would probably give rise only to quasi-elastic scattering, since it is probable that the short range ordered regions are not completely stable with time. These regions, of course, would correspond to the well known tweed phenomena [15] often observed in alloys, but not in pure materials. One may consider that such a short range ordered phase is equivalent to the spin-glass phase, much discussed in magnetism. Damping effects are observed[13] for the excitations (spin waves) in spin-glasses in the quasi long-ranged-ordered high temperature (ferromagnetic) phase, which probably corresponds to the high temperature bcc phase in the Martensitic case for the alloys. The interesting analogy between the Martensitic and the spin-glass problems was recently pointed out by Kartha et al [14], although in a slightly different form and context.

4. CONCLUSION

We have introduced a simple disorder-scattering theory and shown that it can account for the observed large depression of the Martensitic transition temperature in the TiZr alloy system. General comments have been given to the effect that the mechanism does contribute also in other, more complicated cases to a significant dependence of the Martensitic temperature on the alloy concentration. The effect will be largest when the additional alloy element has a very different mass or is chemically very different from the other elements.

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[9] The exact perturbation theories [7], valid for small $c$, consider more complicated phenomena, as localized modes, resonances etc. However, no theory exists for the larger concentration regions, in which we are here primarily interested. Thus we have applied the most simple, physically intuitive, assumptions for describing the dominant effects of the disorder. Experimental tests of these assumptions would be quite interesting. In cases like $Ni_\alpha Ti_{1-\alpha}, x = \frac{1}{2} + \epsilon$ and $Cu_3AlBe_2$, where one is interested in the behavior for small concentration variations $\epsilon$, it may be possible to use the results of the perturbations theories [7] to get more quantitative results than aimed at in this paper. However, the basic disorder scattering mechanism would be the same.
[11] To get the pure limits right for $\langle H \rangle$ we may use a 'coherent potential' approximation for the Greens function for an alloy $A_\alpha B_{1-\alpha}$: $G_\omega = cG_0^A(\omega) + (1-c)G_0^B(\omega)$. This gives an additional $c$-dependence in eq.(5), and introduces the possibility for a skewness of the parabolic form. In the first approximation one expects a simple linear interpolation between the pure $M_\alpha$ temperatures, corrected by the symmetric depression according to eq.(6). However, if the ratios between the disorder and anharmonic scattering scattering power are different for the pure elements - or the Debye temperatures are different (expecting $(k_B\theta_D)^2$ to give a measure for $\sum_q\langle \omega^2_q \rangle$), we will in addition get a factor of the form $(1 + p_c c)$, where $p_c$ is a skewness parameter. This factor is to be multiplied on the left hand side of eq.(6).